Organic Electroluminescent Devices

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Electroluminescence from organic materials has the potential to enable low-cost, fullcolor flat-panel displays, as well as other emissive products. Some materials have now demonstrated adequate efficiencies (1 to 15 lumens/watt) and lifetimes (>5000 hours) for practical use; however, the factors that govern lifetime remain poorly understood. This article provides a brief review of device principles and applications requirements and focuses on the understanding of reliability issues.

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m T}$ he first commercial GaAsP light-emitting diodes (LEDs) were introduced in 1962 (1). Electroluminescence (EL) was reported in organic materials at about the same time, from experiments using both solid (2) and liquid (3) contacts to crystalline emitters as well as liquid emitters with solid contacts (electrochemiluminescence, or ECL) (4). Development of display products was hampered by fabrication and packaging problems and short lifetimes (time to 50% of initial luminance), however, and progress over the next two decades was primarily in the inorganic area. Today, GaAs-based LEDs are available whose efficiency in some spectral regions exceeds that of filtered fluorescent lamps of the same color and is within a factor of 3 of white fluorescent lights.

Although there were a few interim publications (5–7), interest in organic EL was revived mainly by Tang and Van Slyke (8) in 1987 with their multilayer device that uses evaporated films. The first publication describing well-defined polymer EL, by Partridge (7) in 1983, was largely unnoticed, but the work of Burroughs *et al.* (9) attracted more attention. An explosive growth of activity followed in both academia and industry, and Pioneer has announced plans (10) to begin selling a 64-by-256-pixel green flat-panel display in 1996.

Here we will give only a brief introduction to the physics of organic EL; an excellent and comprehensive discussion can be found in a monograph by Greenham and Friend (11). Our emphasis will be on the chemical or materials issues that currently limit the potential for commercial application, and we include some discussion of the competitive context into which such applications must fit.

Device Physics

The basic structure of an organic LED is simple: One or more organic films are de-

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posited in between two electrodes, one of which is transparent. Under a dc bias of ~ 2 to 30 volts, electrons are injected from a low work function ($\Phi_w \sim 3$ to 4 eV) cathode and holes injected from a high Φ_w (~ 5 eV) anode into the organic material, where they travel in the applied field until they meet and form a luminescent excited state. Films may be formed by evaporation, spin-casting (or other polymer film–forming technique), or chemical self-assembly (12). Thicknesses range from a few monolayers (self-assembled films) to about 1000 to 2000 Å.

Thus, the basic requirements for the organic layer are that it be an efficient luminescer and a good charge transporter, and it must be capable of undergoing efficient charge transfer to an electrode. In the following paragraphs we will discuss each of these phenomena in turn.

Luminescence. Excited states formed in typical organic EL materials have photophysical characteristics similar to those in familiar organic chromophores such as laser dyes; indeed, photoluminescence and EL spectra are nearly always identical. The basic structures of a typical molecular emitter, tris (8-hydroxy-quinolinate) aluminum (III) (referred to as Alq₃), and a common EL polymer, poly(phenylene vinylene) (known as PPV), are shown in Fig. 1. Structural variations yield different colors, and white-light devices have been fabricated by using suitable combinations (13).

A common set of photophysical concepts satisfactorily describes devices made with evaporated molecules, fully conjugated polymers, polymers with short conjugation lengths, and nonconjugated polymers with electroactive groups appended. Excitation transport along chains is facile and leads to emission mainly from the longest conjugation lengths (which are generally not more than 10 to 15 monomers). Excitons also move (less rapidly) from one chain (or molecule) to another; energy transfer to "dopant" dyes is often used to obtain other colors (14) and greater stability (15). In PPV (which has no side groups to separate the chains), initial excitation rapidly decays to an interchain exciton that is apparently nonradiative, although it can revert to the radiative intrachain state (16).

Charge transport. Charge moves by electron transfer reactions, or hopping, between molecules (17). Even along a polymer chain, conformational disorder interrupts the idealized one-dimensional transport. Tunneling through σ bonds is far more efficient than through space (18), so intrachain transport is expected to be faster than interchain transport. Nevertheless, the mobility in polymers ($\sim 10^{-4}$ to 10^{-8} cm² V⁻¹ s^{-1} for holes) is typically smaller than in molecular glasses ($\sim 10^{-2}$ to 10^{-5} cm² V⁻¹ s^{-1}) (19). Mobilities for electrons, which are believed to be easily trapped by sites containing oxygen, are even lower (20). These low values are presumably a reflection of both poor wave function overlap in amorphous systems and trapping, and they can have important ramifications for LED efficiency, as discussed below.

Charge injection. Cathode materials include Ag and Al ($\Phi_w = 4.3 \text{ eV}$) (21), In ($\Phi_w = 4.1 \text{ eV}$), Mg ($\Phi_w = 3.7 \text{ eV}$), Ca (Φ_w = 2.9 eV), and others, and anode materials are usually Au ($\Phi_w = 5.1 \text{ eV}$) and indium tin oxide (ITO) ($\Phi_w \sim 4.7 \text{ eV}$). Parker (22) surveyed these and other materials and found excellent consistency with a tunneling model in which the barrier was determined solely by the metal Φ_w and the energy levels of the polymer {poly[2-methoxy,5-(2-ethylhexoxy)-1,4-phenylene vinylene] (MEH-PPV)}. An extremely good fit to a plot of log η_{el} (quantum efficiency, photons per electron) versus cathode $\Phi_w^{3/2}$ was obtained for metals from Ca through Au. He also found a relatively weak temperature dependence of the current. Other studies (23, 24), however, have implicated thermal injection near the device turn-on and thermally assisted tunneling at higher fields. Considering that Parker's Fowler-Nordheim plots approach linearity only at the highfield extreme (where the temperature depen-



Fig. 1. Basic structure of tris (8-hydroxy-quinolinate) aluminum (III) (Alq_3) (left) and poly(phenylene vinylene) (PPV) (right).



dence was measured), these results may not be inconsistent. A recent analysis by Davids and Smith (25) suggests that tunneling dominates only for large barriers (several tenths of an electron volt), with a strong contribution of charge backflow because of the very low mobility [a concept suggested also by Vestweber *et al.* (23)]. For smaller barriers, space-charge–limited thermionic injection is dominant. For TPD/Alq₃ devices (having a layer of TPD and a layer of Alq₃), Burrows and Forrest described the current-voltage behavior as space-charge–limited current in a trap-filled insulator (26).

Analyses that depend on Φ_w , typically measured on clean surfaces in ultrahigh vacuum, must consider the fact that surface adsorbates typically give shifts in Φ_w of \sim 0.1 to 1.5 eV (27). The behavior of the commonly used cathodes evaporated onto conjugated polymers has now been extensively studied (28). In general, it is observed that Al forms covalent bonds with the polymer, and Ca undergoes charge transfer, forming ionic Ca and bipolarons (doubly charged ions) in the polymer. Only one (theoretical) study has been reported for Mg, suggesting that interaction with π -conjugated polymers is weak at most. The transition metal carbide ZrC has $\Phi_w = 3.6$ eV and is stable in air (29). However, the η_{el} of an Au/MEH-PPV/ZrC device (30) is well below that obtained with Al as the cathode. Although the possibility of improvement is not yet ruled out, the data are reproducible and similar for several samples and provide significant evidence that Φ_w alone cannot account for the charge injection barrier in organic LEDs.

Regardless of these details, high fields are required because the voltage drop appears across the entire active region. If the film is made conductive (such as by electrochemical doping), the charge carriers cause quenching of luminescence (11). In ECL, electrolyte counterions equalize charge and yield a non-zero field only at the interfaces. Changes in the external bias move the Fermi level of the metal until it lines up with the energy of the adjacent molecules; hence, efficiency is no longer affected by the electrode Φ_w . Considerable effort was expended during the late 1960s and early 1970s toward the development of ECL displays; lifetime issues prevented commercial success (31). ECL was demonstrated in MEH-PPV in contact with an electrolyte solution in 1994 (32), and the availability of solid-state polyelectrolytes has led to a resurgence in interest in this technique (33).

Carrier injection balance. Single-layer devices tend to produce unbalanced charge injection and lower efficiency. To prevent this, a charge transport or injection layer (for either holes or electrons, or both) is used (compare Fig. 2). This has two effects: (i) it may lower the barrier at the electrode, and (ii) a proper choice of orbital offsets between the layers can block the transmission of the majority carrier, creating a space charge that reduces its current and balances the charge transport. This poses some challenges for polymers, because the upper layer must be cast without redissolving the lower one. Although less obvious, it may also be a concern for evaporated films, because interdiffusion of the layers may occur either during deposition or later in operation (34).

Applications and Design Goals

Inorganic emissive display sources. The development of LED efficiency since the early 1960s is illustrated in Fig. 3. Organic devices have improved rapidly since their introduction, and this comparison suggests that they have much room left.

Several other emissive technologies exist, which have been reviewed recently by Moon (1). The most prevalent of these today for small flat-panel displays is based on vacuum fluorescence, which is essentially a flattened cathode ray tube. The luminous efficiency is about 1 lm/W, and drive voltage is 30 to 50 V. Flat-panel displays are long-lived and rugged; however, larger sizes require supports to prevent window collapse, which increases cost. Plasma displays (which use phosphors for multicolor operation) do not face this limitation and are similarly long-lived, but they operate at even higher voltages (100 to 200 V) and attain lower efficiencies (~0.2 lm/W); color operation lowers efficiency further. EL from II-VI compounds (for example, Mn-doped ZnS) is obtained from an all solid-state device with 2 to 5 lm/W for orange-yellow light (ac driven), which, however, requires 200- to 300-V bias and is not available in all colors at reasonable efficiencies. All of these systems except plasmas have some difficulty achieving good uniformity over large areas. Field emission displays (similar to vacuum fluorescence but with cold cathodes) are under development but have not reached the market.

Polymer-dispersed liquid crystals (PDLCs) with backlighting from vacuum fluorescence represent another important competitor (35). Conventional liquid crystals (which make up \sim 85% of the current flat-panel display market) suffer both from substantial driver costs (for active matrix systems) and low efficiency



Fig. 2. Schematic energy diagram for a bilayer device that uses a hole transport layer [TPD = N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1-biphenyl-4,4'-diamine). The energies of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) in TPD are higher than in Alq₃, producing a bottleneck at the interface and reducing the fraction of current that fails to undergo recombination. The electrode energies are approximate work functions. ΔE_A and ΔI_P are differences between LUMO and HOMO states, respectively.



Fig. 3. Progress in LED efficiency modified from Craford (59). Note that inorganic LEDs can operate at current densities ~1000 times those of OLEDs.

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(because the polarizing optics waste up to 85 to 90% of the light); PDLCs do not require polarization. They currently require voltages of ~ 10 to 20 V.

Inorganic LEDs would seem ideal in all respects: They have excellent η_{el} , bias of only a few volts, availability in all colors, and superb reliability. There is only one major problem—cost. Displays must be assembled from individual color-matched LEDs into the correct position and wire bonded; this is prohibitive for more than about 10 to 15 characters (5 by 7 pixels each).

Applications and requirements. Displays can range in complexity from a single pixel (such as an instrument lamp or a picture) to a high-resolution computer monitor (currently 1.3×10^6 three-color pixels). The luminance of a cathode ray tube is ~100 cd m⁻². Power efficiency requirements are more severe if the display is to be battery-powered and if it is to be used outdoors. Bias voltage should be compatible with the battery (≤ 9 V) to avoid the cost of voltage upconverters.

Lifetime and environmental specifications also differ according to usage. A desktop display should have an operating lifetime of at least a few years but will typically reside in a temperature-controlled environment. Portable appliances, on the other hand (such as cellular phones or palmtop computers), may be off during much of the product life, but they must withstand extremes of temperature and humidity and, more or less frequent, relatively rapid cycling between extremes. Manufacturers usually specify somewhat more severe demands than are expected to be actually met in the field to guarantee high reliability, and storage at up to 85°C (and down to -40°C) is desirable; 70°C and -30°C are probably essential. Although operation will not normally be at these extremes, the degradation of lifetime with temperature during operation must be small. Because of the severe sensitivity to water and oxygen, hermetic packaging techniques are required that must also be stable under these conditions. Although the hermeticity requirement may be greater for organic LEDs (OLEDs), most other systems, including liquid crystals, require similar sealing.

From these considerations, the appropriate near-term target for OLEDs is most likely displays of ~10 to 1000 characters. (Although greater pixel counts may someday be practical, the difficulties are formidable, especially for full-color displays, and much work needs to be done to assess them.) Considering commercial surveys of the market fraction that could be taken away from other technologies, it is projected (1) that these applications may amount to about \$1 billion in OLEDs by 2001. "Novel" applications of OLEDs, emphasizing, for example, the potential for flexibility (especially with polymers), could lead to larger markets, but details are speculative at this point.

Monochrome operation will be acceptable for these initial applications, but fullcolor operation is desirable and eventually essential. There are three ways of achieving this: (i) evaporation at selected angles against walls of different heights to determine the spatial distribution of compositions emitting different colors (36); (ii) construction (by plasma etching) of Fabry-Perot microcavities whose length determines the emission wavelength from a white-lightemitting composition (37); and (iii) downconversion of blue emission to green and red by means of energy transfer to dyes in a 'color conversion layer" interposed between the emitter and ITO (38, 39).

Reliability Issues

Efficiency, drive voltage, and color selection had attained adequate levels for commercialization soon after the introduction of OLEDs. However, the device lifetimes were far from adequate. Today, lifetimes in the range of 5000 to 35,000 hours at a starting level of 200 cd m^{-2} are being reported (15) for evaporated films, and >5000 hours for the best polymers (40). These values are for room temperature and in the absence of water and oxygen, and are extrapolated on the basis of the (generally valid) assumption that lifetime is inversely



Fig. 4. EL in an ITO/TPD/Alq₃ plus quinacridone/Mg device operated in N_2 at 100% relative humidity (3% H₂O). The device is 2 mm wide.

proportional to current density. Few publications devoted to reliability issues have appeared (41–45), however, and nearly all polymers reported are well below these values, as are many molecular devices. We review here some experiments that relate to potential mechanisms of degradation of OLEDs. We use MEH-PPV as a prototypical polymer and TPD/Alq₃ as the molecular system because of their ready availability and good initial performance (voltage and efficiency), although the lifetimes achieved have not been the best reported.

Reactions with water and oxygen. As mentioned above, OLEDs use low Φ_w cathodes, generally Mg or Ca, that are susceptible to oxidation by either water or O₂. Figure 4 shows circular black spots (41) in a TPD/ Alq₃ (quinacridone-doped) device that grow in the presence of H_2O but not in N_2 , negligibly if at all in O_2 , and independent of operation. Photoluminescence (PL) from these spots is slightly brighter than elsewhere; if the electrode is peeled off with tape, the PL becomes uniform (46). Under a Nomarski microscope the spots are seen as elevated bubbles in the electrode. These experiments show that the black spots are regions of water-induced delamination, probably associated with pinholes (46). Papadimitrakopoulos et al. (47) described some reactions of Alq₃ in the presence of



Fig. 5. *L-I-V* curves for ITO/X/MEH-PPV/Ca devices, where (**A**) X is no layer (direct contact of ITO to MEH-PPV), and (**B**) X is a 25% PANI-75% polyester blend (the MEH-PPV solution dissolves the polyester and fills the resulting pores with MEH-PPV). The same spinning conditions were used for both MEH-PPV films.

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 H_2O and O_2 ; we do not yet know if they occur in devices.

Calcium reacts much faster than Mg; an ITO/PANI/MEH-PPV/Ca (~2000 Å) device (where PANI is polyaniline) operated in H₂O vapor loses 90% of its efficiency (but only one-third of its current) in 37 s. The electrode is far from fully oxidized; it still appears shiny and opaque. In order for most of the device to be affected in only 37 s, one must assume that the metal (unlike Mg) has a highly porous morphology near the interface.

Several authors examined photodegradation in conjugated polymers, including PPV (48) and poly(2,5-bis(5,6-dihydrocholestanoxy)-1,4-phenylenevinylene) (BCHA-PPV) (49, 50). Scurlock et al. (49) confirmed singlet oxygen participation in BCHA-PPV, though the monomeric analog stilbene does not react with ${}^{1}\Delta O_{2}$. $\pi 2 + \pi 2$ cycloaddition gives rise to aldehydes, which have been observed by means of Fourier transform infrared spectra in the photolysis of PPV (48) and in BCHA-PPV (50). Holdcroft and co-workers (51) also identified ${}^{1}\Delta O_{2}$ in the photodegradation of poly(3-alkylthiophenes). Scott et al. (45) presented evidence that ITO may be a source of oxygen. Rapid and complete chain degradation is observed: A 1500 Å film of MEH-PPV irradiated with $\sim 25 \text{ mW cm}^{-2}$ (380 to 425 nm) for a few hours disappears. Under high vacuum, however, BCHA-PPV has a photobleaching quantum yield of $\sim 3 \times 10^{-9}$. We find the photobleaching of Alq₃ to be more than 10 times slower, but still fast enough that complete exclusion of O_2 from devices is required.

Temperature stability. As mentioned earlier, commercial displays (especially ones to be used in portable devices) must withstand extremes of temperature and thermal cycling. In our preliminary studies, we have found a lifetime reduction of about a factor of 20 for an ITO/PANI/MEH-PPV/Ca device operated at 60° compared with 30°C. ITO/PANI/TPD/Alq₃/Mg decay is also accelerated by temperature, but the dependence has not yet been quantified. Power dissipation above \sim 500 mW cm⁻² leads to significant internal heating.

The use of the starburst amine (52) 4,4',4"-tris(3-methylphenyl-phenylamino)triphenylamine, which has a higher glass transition temperature than TPD, as a hole transporter appears to improve thermal stability and device lifetime. Tang and coworkers have also reported hole transporters of high stability, using naphthyl in place of one phenyl in the TPD structure (15). Crystallization of TPD (53) and intermixing of Alq₃ and TPD layers (34) have been observed; however, the relation of these events to device degradation remains undefined. At this time there is no published work on the mechanisms of thermally activated degradation pathways.

Electrode materials and processing. Direct lifetime comparison between Ca and Al is problematic because of the larger bias for Al. However, the lifetime in N_2 of ITO/ PANI/MEH-PPV/M devices is not greater when M is Ag than when it is Al, and both are much less (by much more than an order of magnitude) than with Ca (which is 100 hours at 33 mA cm^{-2} in a typical run). In addition, ITO/MEH-PPV/Alq₃/Ca devices, which have greater η_{el} than ITO/MEH-PPV/Ca, have similar lifetimes. Thus, cathode reactivity does not appear to be a limit to device lifetime in this set of materials. Should the lifetime-limiting factors in these experiments be eliminated, it is not ruled out that cathode reactivity could become an issue at longer times.

The effect of the conducting polymer

PANI on the light output and current as a function of bias (L-I-V curves) (54) is shown in Fig. 5. The noisy "dark" current seen with bare ITO is typical, and these devices die by shorting well before decaying to 50% output (45). With PANI, not only is the η_{el} greatly increased (54, 55), but the I-V curve is now monotonic, and most such devices decay smoothly without shorts. An even more dramatic effect is seen with evaporated films. ITO/TPD/Alq₃/Mg consistently shorts almost immediately in N2 (although it may survive for several tens of hours in air); with ITO/PANI/TPD/Alq₃/ Mg the lifetime in N_2 is extended to several hundred hours (56). This behavior suggests that shorting (and the leakage current) is in many cases connected to particles, which are probably covered by the PANI.

Interface studies. To better understand surface effects, we prepared ITO substrates treated with various alkyl silanes (57), which are known to produce chemisorbed monolayers or ultrathin multilayers under the right conditions. An excellent correlation of η_{el} with surface energy γ is shown in Fig. 6, with the best results obtained for the lowest energy (matching MEH-PPV, ~27 dynes cm⁻¹). However, bare ITO does not lie on this line, nor does PANI (0.9 cd A⁻¹, 52 dynes cm⁻¹). There is also a smooth variation of field with γ , but the minimum does not match MEH-PPV, and it does not agree with the η_{el} plot.

For vinylsilane, very good *L-I-V* curves were obtained (similar to PANI, although still not as efficient), showing that a monolayer is sufficient to substantially reduce the leakage currents seen with bare ITO. However, these devices had a tendency to short that was not only worse than with PANI, but even worse than with bare ITO (lasting



Fig. 6. Surface energy γ (obtained from water contact angles) versus efficiency η_{el} or electric field ${\it E}$ for ITO/X/MEH-PPV/Ca devices, where X represents ultrathin layers of organosilanes.



Fig. 7. AFM image of the impression left by lowering a Pt/Ir STM tip at 10-V bias and 110pA current setpoint onto an MEH-PPV film (750 Å thick) on ITO, with zero scan size. a few hours or less). There was no improvement of lifetime or efficiency for TPD/Alq₃ devices on any of the modified substrates listed. Although there is much to be clarified in these observations, they establish that (i) the particle-dependent shorts can be affected by ultrathin layers (which presumably also coat the particles), and (ii) injection efficiency can be modified in complex ways by interface modifications.

Another approach to surface characterization is by scanning probe microscopies, including both scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Images of ITO from the two techniques are essentially identical, showing that there are no inhomogeneities in surface conductivity over distances greater than 100 Å. Electrode roughness does not correlate with device behavior.

More interesting are STM studies of the emitting polymer surface. Tunneling can be obtained in MEH-PPV with a standard (albeit rather blunt) STM tip (Fig. 7). Three measurements were made by letting the tip approach the sample with bias setpoints of 10, 8, and 4 V (always at 110-pA current); deeper indentations (hence a thinner film) are obtained with smaller setpoints. After recording I-V curves, the depth and area are found from AFM images, thus yielding current density versus applied field. All three give a field of 4.0×10^5 V cm⁻¹ for a forward current (tip negative) of 5 mA cm⁻², which can be com-pared with 1.2×10^6 V cm⁻¹ for devices (22) with evaporated cathodes of high Φ_w metals such as Cu or Au. The precision of these measurements needs to be refined; nevertheless, they already show that I-V characteristics of conjugated polymers (and presumably EL molecular films as well) can be obtained on a microscopic lateral scale with STM. This opens up several avenues of research: (i) the comparison of cathodes with different Φ_{w} 's, with little or no chemical reaction; (ii) an analysis of the effects of evaporation (which presumably leads to a metal-polymer interface with a significant, and varying, degree of diffuseness); and (iii) an exploration of lateral inhomogeneity in the conductivity of the organic material.

Chemical purity. It is a maxim in the fabrication of inorganic LEDs that higher material purity is always better. Organic systems are not immune from this concern; a dramatic example was afforded by our observation that coevaporation of $0.5\ wt\%$ quinacridone (98% nominal purity) with Alq₃ dropped the lifetime of a TPD/Alq₃ device by a factor of 10⁴ compared with sublimation-purified quinacridone, as well as reducing somewhat the initial efficiency.

It is important to realize, however, that the basis of the need for purity differs between inorganic and organic devices. The

former are invariably well-ordered crystals, and virtually any crystal defect can interfere with both efficiency and lifetime. The latter are amorphous, and chemical components may be functional, detrimental, or neutral according to their energetics (58). An example of an important impurity in an EL polymer is the carbonyl group in oxidized PPV (20, 48). On the other hand, polymers whose transport of holes is trap-free (and hence impurity-free for the intended function) are well known in electrophotography (20, 58), and polymer-based charge carriers have long played a key role in the electrophotography industry (58). Absolute chemical purity is more difficult to approach in polymers than in low molar mass molecules, but the degree to which this may affect their application in EL remains to be determined.

Conclusions

Although organic LEDs appear ready to enter the commercial stage, reliability is still a key issue, and a fundamental understanding of how to extend it is only now beginning to emerge. The next few years should see major advances in this area, and the availability of a much wider array of durable materials and processes for the device and system designer than presently exists. With lifetime issues under control, the next focus of research will probably be in the improvement of power efficiency.

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